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Energy Procedia 18 (2012) 733 – 740

Energy Procedia

Effects of thickness and chemical quality of SiO_2 barrier on $POCl_3$ diffusion during the formation of emitter

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Abstract

The distribution of phosphorus dopants in the emitter formed by $POCl_3$ diffusion show an important 'kink' resulting from the existence of electrically inactive phosphorus. Further, this 'kink' participates to form a zone called 'dead layer' and reduces considerably the minority carrier collection in surface. In order to minimize the effects of this layer, a new technique was used. It can be summarized in an addition of a pre-oxidation step before the phosphorus diffusion.

In this paper, we conducted a numerical simulation of phosphorus diffusion by adding a pre-oxidation step, and by varying the chemical quality of silicon oxide SiO_2 (wet or dry). The thickness measurement of SiO_2 layer formed was accomplished by varying several parameters as: pressure, temperature, and diffusion time. Our results show that it is possible to reduce the kink by a dry SiO_2 layer and thickness of 80nm.

Keywords: Silicon solar cells; phosphorus diffusion; thermal oxidation; numerical simulation; diffusion profile.

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 doi:10.1016/j.egypro.2012.05.089

1. Introduction

In the industry, the emitter formation is the most critical step during the fabrication of the standard crystalline silicon solar cells. Different techniques are used: spray, spin on dopants/glass, screen printing and the most widespread $POCl_3$ diffusion…. By using this technique, the formed emitters present a heavy concentration of phosphorus doping on the surface which causes an important recombination of the minority carriers. Some manufacturers tried to reduce the heavy inactive phosphorus concentration on the surface and the thickness of the dead zone by a better control of the physical and technological parameters of the diffusion (pressure, mass flow of gases, temperature, time…). Unfortunately, that was impossible and the only alternative is to grow barriers diffusion by using the silicon oxides or the silicon nitrides. [1, 2]

In our numerical simulations accomplished by using the ATHENA-SILVACO Software, the growth kinetics of silicon oxide is described by the model of Deal and Groove [3] for special conditions of pressure and temperature. The estimation of the barrier diffusion thickness is carried out for silicon dioxide both: dry and wet, and the effects of diffusion parameters are investigated in our paper.

2. Numerical simulation

The starting silicon substrate has a known thickness. With the increase of the temperature and under an oxygen flow, a film of silicon oxide begins to be formed. A simplified diagram for the growth kinetics of silicon oxide film can be presented as:

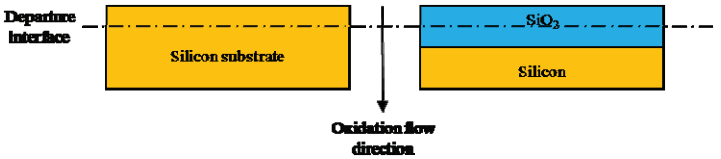

Fig. 01: Diagram of growth kinetics of SiO_2 from a silicon substrate.

Then, under the influence of $POCl_3$ flow, the formation of emitter is obtained by phosphorus diffusion into substrate. The SiO_2 layer formed during the pre-oxidation step is considered as barrier for phosphorus diffusion.

2.1. Effects of oxidation

The phosphorus diffusion profile in the crystalline silicon defines the distribution of dopant in the crystalline matrix. Mathematically, this distribution is deduced after resolution of the second equation of Fick, and it is function of time, temperature and phosphorus concentration [4].

However, it was shown experimentally a great influence of oxidizing atmosphere on the evolution of the diffused dopant. In particular, an oxidizing environment involves generally an enhancement of diffusion of phosphorus (OED) and a deceleration of antimony diffusion (ORD) [5].

The phosphorus diffusion in the oxidizing environment can be described as a function of the ratio of equilibrium concentration of dopant in silicon and it oxide (SiO_2), and also the diffusion coefficient in both matrices.

The mode of oxidation is defined according to the source of oxygen, two modes can be defined:

2.1.1. Dry Oxidation

It is characterized by an O_2 flow, which is added to the flow of gas doping introduced into the furnace. The chemical reaction between silicon (solid) and oxygen (gas) is:

$$Si + O_2 \rightarrow SiO_2 \quad (1)$$

This oxidation mode gives a better quality of formed oxide.

2.1.2. Wet oxidation

In this case, silicon wafers are subjected in addition to the oxygen flow to a vapor flow (H_2O). The chemical reaction is:

$$Si + 2\,H_2O \rightarrow SiO_2 + 2\,H_2 \quad (2)$$

Because of its water content, the oxide films formed by wet process have a more important porosity than those formed by dry oxidation. The wet oxidation is more rapid which is considered as the ultimate advantage of this technique.

In our numerical simulation carried out by using the ATHENA-SILVACO Software [6], we accomplished a phosphorus diffusion by adding a pre-oxidation step and by varying the atmosphere of diffusion (wet or dry) under a temperature about 825°C and during one hour. Several cases are present according to environment inside the diffusion tube. On the graph below, the influence of atmosphere on the diffusion profiles is obvious. Nevertheless, the important cases under humid atmosphere are marked by an acceleration of oxide layer formation, result of additional oxygen present in the flows of vapor water and O_2 flows introduced into the quartz tube.

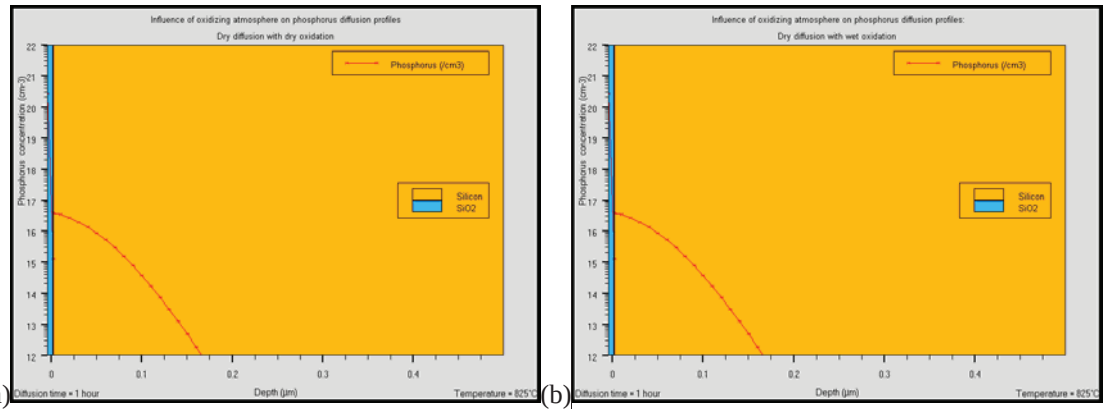

Fig. 2: Influence of oxidizing atmosphere on phosphorus diffusion profiles: (a) Dry diffusion by adding a dry pre-oxidation step. (b) Dry diffusion by adding a wet pre-oxidation step.

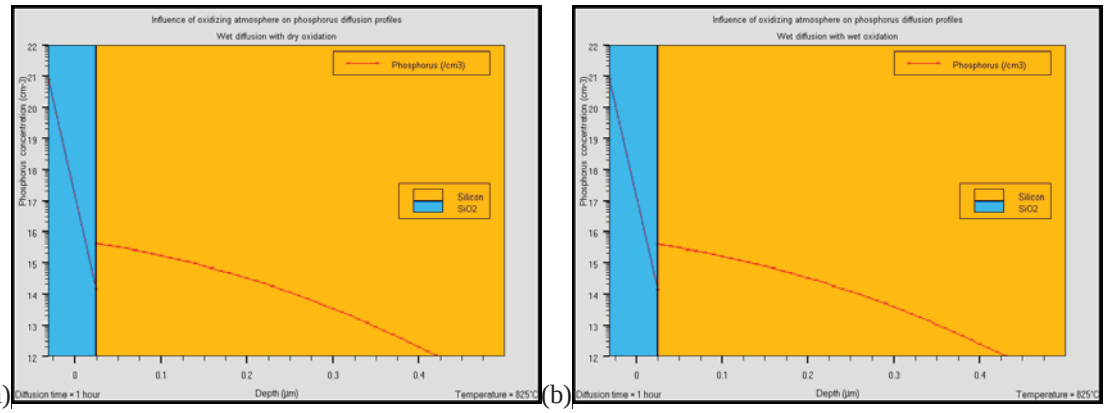

Fig. 3: Influence of oxidizing atmosphere on phosphorus diffusion profiles: (a) Wet diffusion by adding a dry pre-oxidation step. (b) Wet diffusion by adding a wet pre-oxidation step.

2.2. Estimation of oxide layer thicknesses

At room temperature, silicon has a natural tendency to form an oxide layer. This feature makes the thermal oxidation process simple to implement. The principle of thermal oxidation consists in bringing an external excitation by heat to support the transport of species. A mathematical formulation of silicon oxidation has been proposed for the first time by the Deal and Groove model which is still the most relevant one and the basis of many other works. [3]

We carry out our numerical simulation of phosphorus diffusion in the single crystalline silicon initially doped boron at 10^{16} cm^{-3} under an atmospheric pressure. The temperature of process is about 825°C and the time of process is one hour. The surface phosphorus concentration considered is equal 2.10^{22} cm^{-3}. This diffusion is preceded by a wet or dry oxidation to study their influence on the growth kinetics. The table below resumes the calculations of the thickness obtained by different oxidation and diffusion.

Table 1: Thicknesses of the oxide layer formed expressed in (A°)

Process	Dry oxidation	Wet oxidation	Standard diffusion process without pre-oxidation step
Dry diffusion	72.8	72.8	72.8
Wet diffusion	562.0	567.5	561.6

These results clearly show the influence of wet oxidizing atmosphere on thickness of silicon oxide formed. In the following step, we will study the influence of phosphorus diffusion parameters on the thickness of the oxide layer.

2.3. Influence of diffusion parameters on oxide layer thickness

A calculation of the SiO_2 layer thickness formed was taken while varying several parameters: pressure of the tube, temperature and diffusion time.

2.3.1. Pressure

The variation of pressure in the diffusion tube furnace was carried out from 0.1 to 1 atm with a fixed temperature at 825°C and during 60 minutes of process time. The figure 4 illustrates the variation of oxide layer thickness versus pressure for a wet pre-oxidation case.

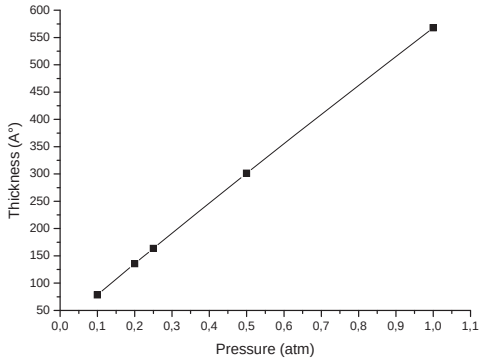

Fig. 4: Variation of oxide layer thickness with pressure of diffusion tube furnace for a wet pre-oxidation.

At low pressure, the thickness of SiO_2 is less than 100A°. A linear behavior of curve is observed and the thickness can achieve 570A° after one hour of process.

The thickness of silicon oxide increases with pressure in the furnace for dry and wet oxidation in the same way. The main advantage with the increase of pressure is the temperature necessary to the diffusion which is almost divided on half.

2.3.2. Temperature

To explore the effect of temperature, diffusion under humid atmosphere with pressure about 0.2atm and preceded by a wet oxidation step during 60 minutes was carried out.

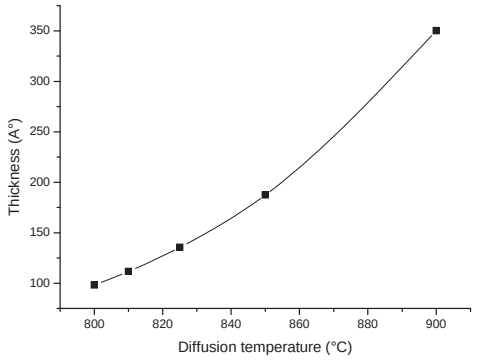

Fig. 5: Variation of oxide layer thickness with temperature of diffusion tube furnace for a wet pre-oxidation.

The rate of oxidation increases significantly with the temperature in the furnace for dry and wet oxidations. In case of a wet oxidation, it is noticed that an increase in temperature about 50°C leads to approximately the double thickness of SiO_2 formed. The great influence of temperature on the formed oxide layer is explained by the influence of temperature on diffusivity of oxygen and the H_2O in silicon.

2.3.3. Time influence

To study the influence of the time parameter, we suppose a constant time of phosphorus pre-deposition and we vary the drive-in time (redistribution of impurities) [8] under a temperature of 825°C.

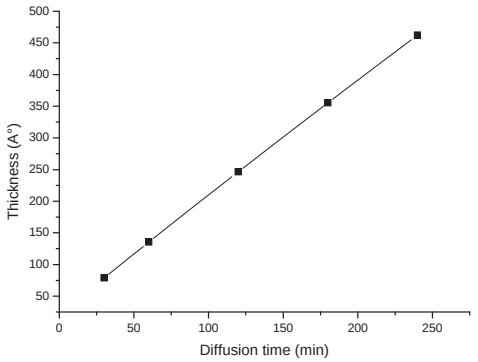

Fig. 6: Variation of oxide layer thickness with diffusion time for a wet pre-oxidation.

The influence of drive-in time on the oxide thickness has a linear form, but it is allowed that deep junctions require a longer time of diffusion. This is directly related to electric characteristics of emitter. [8]

3. Effects of SiO_2 barrier diffusion

The influence of phosphorus diffusion parameters on the variation of the oxide layer thickness during emitter formation is investigated. The thermal oxidation process has the advantages of being easily used by photovoltaic industry. The quality of manufactured device, their performances and reliability strongly depend on conditions development of oxide layer. The process must thus be thoroughly controlled in order to obtain the best possible emitter.

We propose to study the influence of addition of a wet oxidation step before phosphorus diffusion. We obtain a panel of emitters of various sheet resistances. Then, we analyzed them and a relation between the time of the pre-oxidation and the doping of the emitter has been demonstrated.

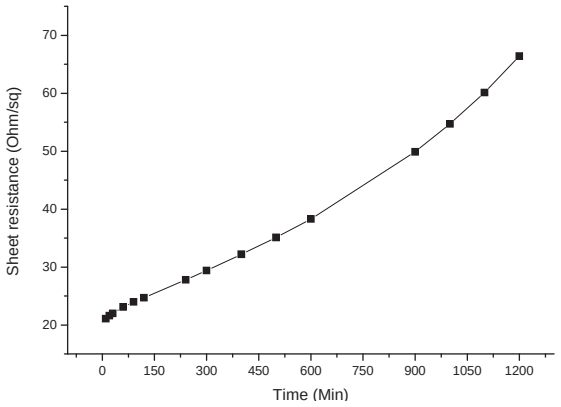

Fig. 7: Emitter sheet resistance variation versus pre-oxidation time

The formation of thermal oxide causes an increase in sheet resistance of emitter. The influence of diffusion parameters on the dead layer is demonstrated, while keeping the values of sheet resistance acceptable for the photovoltaic industry.

4. Discussion

This study showed the influence of phosphorus diffusion parameters on the characteristics of the formed emitters. A great influence was observed by adding a pre-oxidation step on the doping of emitter and an evolution of dead layer with diffusion parameters was demonstrated, which led us to conclude a direct relationship between thermal oxidation and quality of formed emitter.

The dead layer is inversely proportional with oxide layer thickness, and an increase in sheet resistance is observed with pre-oxidation time.

The profiles are lengthened under humid atmosphere of diffusion, which gives to think that formed junctions are deeper. The presence of oxygen has reduced electrically inactive phosphorus used for dead layer formation.

Thicknesses evaluation of formed oxide layer led us to better understanding the influence of diffusion parameters on the thermal oxidation. Our results are well in correlation with [2] and [9] where some of these authors suggested chemical etching after phosphorus diffusion to reduce dead layer. The method of oxidation brings back to the same results but it has the advantage of no additional step requirement during industrial process for solar cells manufacturing, which makes it simpler and easy to be introduced into photovoltaic industry.

5. Conclusion

During the emitter formation and at high phosphorus concentrations, precipitates are formed on silicon surface and support the existence of electrically inactive phosphorus which forms the dead layer characterized by a kink on the experimental profiles. This high concentration, even if it promotes the realization of ohmic contacts by screen printing. It limits effect of passivation by deposition of antireflects layers.

Many authors suggested an addition of a pre-oxidation step before phosphorus diffusion in order to reduce the dead layer. Control of parameters of diffusion furnace as well as influence of growth kinetics of silicon oxide is necessary in order to optimize as well as possible the phosphorus diffusion in silicon.

In this work, it was shown that the diffusion of the doping agents in silicon is strongly affected by oxidizing atmosphere of diffusion tube furnace, in particular, an oxidizing atmosphere generally involves an acceleration of phosphorus diffusion and it is more important for an oxidation in wet atmosphere than for a dry atmosphere. The method of adding a pre-oxidation step before diffusion is better for a good control of the formation of the emitter.

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